

FORM PTO-1390 (REV 10-95)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				P-3530.001	
				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <b>09/623785</b>	
INTERNATIONAL APPLICATION NO. <b>PCT/GB99/00491</b>		INTERNATIONAL FILING DATE <b>15 FEBRUARY 1999</b>		PRIORITY DATE CLAIMED <b>10 MARCH 1998</b> <b>7 DECEMBER 1998</b>	
TITLE OF INVENTION <b>GASKET COATING</b>					
APPLICANT(S) FOR DO/EO/US <b>ATKINSON, Alan W., BOND, Stephen P., and TURLAND, Darryl A.</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <b>NO DRAWING FIGURES</b></p> <p style="margin-left: 20px;">a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> has been transmitted by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</p> <p style="margin-left: 20px;">b. <input checked="" type="checkbox"/> have been transmitted by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 20px;">d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <b>*TO FOLLOW AT A LATER DATE</b></p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>					
Items 11. to 16. below concern document(s) or information included:					
11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.					
12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.					
13. <input type="checkbox"/> A FIRST preliminary amendment.					
<input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.					
14. <input type="checkbox"/> A substitute specification.					
15. <input type="checkbox"/> A change of power of attorney and/or address letter.					
16. <input checked="" type="checkbox"/> Other items or information:					
PCT/IPEA/416 - 5 PAGES INTERNATIONAL PRELIMINARY EXAMINATION REPORT					
PCT/ISA/210 - 4 PAGES INTERNATIONAL SEARCH REPORT WITH CITED REFERENCES 37 C.F.R. 1.10*					
<input checked="" type="checkbox"/> as "Express Mail Post Office to Addressee" Mailing Label No. <u>EL078272094US</u> (mandatory)					
<i>Nicole R. Schmolitz</i> Signature Nicole R. Schmolitz (type or print name of person certifying)					
Date: <u>September 8, 2000</u>					

U.S. APPLICATION NO. (if different from PCT No.) <b>09/1623785</b>		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
17. <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</b> Search Report has been prepared by the EPO or JPO .....  International preliminary examination fee paid to USPTO (37 CFR 1.482) <b>840.00</b> <del>\$130.00x</del>  No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... \$750.00  Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$970.00  International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$94.00  <p align="center"><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b></p>				CALCULATIONS          PTO USE ONLY	
				<b>\$</b>	<b>840.00</b>
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				<b>\$</b>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	<b>14 - 20 =</b>	<b>0</b>	<b>x18.00</b>	<b>\$</b>	
Independent claims	<b>2 - 3 =</b>	<b>0</b>	<b>X 578.00</b>	<b>\$</b>	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)	<b>7</b>		<b>+260.00</b>	<b>\$</b>	<b>260.00</b>
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$</b>	<b>1,100.00</b>
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				<b>\$</b>	
<b>SUBTOTAL =</b>				<b>\$</b>	<b>1,100.00</b>
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				<b>\$</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$</b>	<b>1,100.00</b>
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				<b>\$</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$</b>	<b>1,100.00</b>
				Amount to be refunded	<b>\$</b>
				charged	<b>\$</b>
<p>a. <input checked="" type="checkbox"/> A check in the amount of <b>\$ 1,100.00</b> to cover the above fees is enclosed. CHECK NO. 17158</p> <p>b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>12-0755</u>. A duplicate copy of this sheet is enclosed.</p>					
<p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p>					
SEND ALL CORRESPONDENCE TO: <b>Robert L. Stearns</b> <b>Reising, Ethington, Barnes,</b> <b>Kisselle, Learman &amp; McCulloch, P.C.</b> <b>5291 Colony Drive North</b> <b>Saginaw, Michigan 48603</b>			 <hr/> SIGNATURE  <u>Robert L. Stearns</u> <hr/> NAME  <u>36,937</u> <hr/> REGISTRATION NUMBER		

## GASKET COATING

This invention is concerned with a gasket coating. In particular, the invention is concerned with a gasket coating for application to a surface of a gasket to provide improved sealing by filling small cracks and fissures in the surface of the gasket and/or of the member against which the gasket seals.

Gaskets are used for sealing between two members, eg two portions of the exhaust system of an internal combustion engine, and provide a seal around a passage which passes from one member to the other. Accordingly, a gasket has to be resilient in order to press against the members and provide a fluid-tight seal. In the case of an exhaust gasket, the seal is to prevent escape of exhaust gases and entry of air. The resilience can be provided by utilising a relatively thick layer of resilient material such as a resilient rubber-based material or graphite but, where high temperatures (above 300°C) are experienced such as in an exhaust system, many resilient materials would degrade and are not commonly used. Instead, the gasket comprises a sheet of metal, eg stainless steel, which is formed into resilient ridges (called "beads") which provide the seal. Thus, when such a gasket is clamped between two members, the clamping force compresses the beads which are resiliently deformed and press against the members along the lines of the beads. However, such gaskets normally do not provide as good a seal as is desirable because the beads are unable to enter into small cracks and fissures in the members so that gases and liquids can escape past the beads. It is known, in gaskets not utilised at such high temperatures as are experienced by exhaust gaskets, to provide metal beads with a thin coating (typically less than 200 microns in thickness) of a sealing-enhancing coating which will deform under clamping pressure to fill cracks and fissures. Known sealing-enhancing coatings, however, degrade at higher temperatures so that they cannot

be used on, eg, exhaust gaskets for internal combustion engines.

It is an object of the present invention to provide a sealing-enhancing coating which is suitable for use on a gasket or a portion thereof, eg exhaust gaskets or bore seals, which will experience high temperatures in service.

The invention provides a sealing-enhancing coating for a gasket or a portion of a gasket, characterised in that the coating comprises flaky particles of chemically exfoliated vermiculite, at least 90% by weight of said particles having a thickness of no more than 30 microns, and no dimension greater than 1mm, the particles forming 10 to 90 wt% of the coating, the coating also comprising 50 to 10 wt% of an organic polymer binder which is heat resistant to at least 300°C.

For the present purposes an organic polymer binder is considered to be heat resistant to a particular temperature if, when the binder is formed into a film 1mm or less in thickness and heated to that temperature in free air for 24 hours, it either does not decompose or decomposes leaving a residue of at least 20% by weight of the film.

It is found that a coating according to the invention improves the sealing ability of gaskets which experience high temperatures in service, in particular gaskets with embossed sealing beads for example exhaust gaskets for internal combustion engines.

Chemically exfoliated vermiculite is a known heat-resistant resilient material which provides sealing and possibly binding properties at high temperatures (eg above 300°C). Exfoliated vermiculite is conventionally formed by expanding mineral vermiculite using gas. Chemically-exfoliated vermiculite (CEV) is a form of exfoliated

vermiculite which is formed by treating the ore and swelling it in water. In one possible preparation method, the ore is treated with saturated sodium chloride solution to exchange magnesium ions for sodium ions, and then with n-butyl ammonium chloride to replace sodium ions with n-C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub> ions. On washing with water swelling takes place. The swollen material is then subjected to high shear to produce an aqueous suspension of very fine (diameter often below 50 microns) vermiculite particles.

It is known to utilise chemically-exfoliated vermiculite in a sealing layer, ie the layer which provides the sealing force by compression thereof, of a sheet gasket, eg an automotive head gasket. For example, GB 2 123 034 B describes making a flexible sheet material, eg for a gasket, by subjecting an aqueous suspension to electrophoresis. The suspension contains an expanded layer silicate, eg CEV with a particle size below 50 microns, and a dispersed organic polymeric material, eg acrylic polymer, acrylonitrile-butadiene copolymer, epoxy resin, or natural rubber. However, these flexible sheet materials are not suitable for use as a sealing-enhancing coating on an exhaust gasket because the polymeric material would degrade at high temperatures and the coating would become less effective.

In a coating according to the invention, the polymer binder is preferably a silicon-containing polymer, eg a silicone resin or a silicate. Also possible are PTFE, phenolics, and fluoroelastomers.

In order to improve the water-resistance of the coating, it is preferred that the coating contains more of the organic polymer binder by weight than of the chemically exfoliated vermiculite.

Preferably, a coating according to the invention also comprises a solid lubricant eg particles of graphite, molybdenum disulphide, hexagonal boron nitride, calcium difluoride, or PTFE (PTFE may also serve as a binder).

A coating according to the invention may also comprise a flaky filler, eg mica, milled thermally exfoliated vermiculite, or aluminium flake. A suitable selection of filler can enhance the drying of the coating after it is applied.

The coating also, preferably, comprises a supplementary inorganic binder/adhesion promoter, eg a water-soluble alkali silicate, especially lithium silicate.

Preferably, a coating according to the invention also comprises a waterproofing agent acting on at least one of the chemically exfoliated vermiculite and supplementary inorganic binders.

Preferably, none of the ingredients of a coating according to the invention should prematurely interact with one another. In particular, none of the ingredients should flocculate the CEV or precipitate the alkali silicate.

Preferably a coating according to the invention has a thickness of less than 100 microns, eg the thickness may be up to 80 microns, eg between 50 and 75 microns.

A coating according to the invention may be used on a bore seal or an embossed steel gasket sheet and is suitable for use in an exhaust gasket of an internal combustion engine.

In order to increase resilience, a coating according to the invention, preferably, has a density of below 70% of

the theoretical density of the material forming the coating. More preferably the density of the coating is below 50% of said theoretical density.

The invention also provides a method of forming a gasket characterised in that the method comprises applying a coating according to the invention to at least a portion of a metal sheet, embossing the metal sheet with the coating to form at least one resilient ridge therein with the coating extending across said ridge, and heating the embossed sheet to a temperature of at least 350°C to temper said sheet. Preferably said metal sheet is made of stainless steel. The coating may be applied to both sides of the sheet, including possibly to both sides of the sheet in the region of the ridge, ie the coating borders the trough created in the other side of the sheet by the formation of a ridge.

There now follows a detailed description of three examples of sealing-enhancing coatings which are illustrative of the invention.

In order to form the first illustrative coating, the following were mixed together:

- (a) 50g of chemically-exfoliated vermiculite suspension (15% solids in water). This was obtained from W R Grace & Co under the designation Microlite HTS. The particles of CEV were flaky and had a size distribution such that at least 90% by weight had a thickness of no more than 30 microns and no dimension greater than 1mm. Specifically, the vermiculite particles have less than 33% above 45 microns diameter and an aspect ratio of at least 100.
- (b) 5g of graphite flake particles (grade Hart 400 from Colin Hart Minerals). This graphite is milled so that

96% of the particles pass through a 37 micron sieve. These particles were included to provide a solid lubricant.

- (c) 5g of aluminium powder (grade Fine 124 from Ronald Britton & Co). The mean particle size of the aluminium is 16-24 microns with less than 1% being retained on a 160 micron sieve. This powder formed a water-proofing agent acting on the inorganic binder(s).
- (d) 5g of mica particles (SX 300 from Microfine Minerals). 1-4% of the mica particles are retained by a 20 micron sieve. The mica was included as an inorganic filler.
- (e) 10g of methyl phenyl silicone resin emulsion (MP 42E from Wacker). This was a suspension in water at 42% solids and provided an organic polymer binder. This resin has an ignition point of 465°C. This binder, when formed into a film 1mm or less in thickness and heated to 300°C in free air for 24 hours decomposes leaving a residue of at least 20% by weight of the film, the residue being silica which has some binding properties.
- (f) 5g of lithium silicate solution (23% solids). This was obtained from Crossfield under designation L40 and provided an inorganic binder in addition to the organic binder provided by the silicone resin and the CEV. The lithium silicate takes over some of the binding function at higher temperatures (at which the silicone resin undergoes thermally-induced chemical changes). The lithium silicate may also promote bonding to steel substrates.

The mixture was sprayed onto the surface of a stainless steel sheet. The mixture was then dried forming



a coating over one surface of the sheet having a thickness of approximately 50 microns. The coating had a density of between 0.7 and 0.8 g/cm<sup>3</sup>, the theoretical density of the material forming the coating being approximately 2.0 g/cm<sup>3</sup>.

Next, the sheet with the coating thereon was embossed to form sealing beads which were covered at their crests by the coating.

Next, the embossed coated sheet was heated to 350°C for one hour to temper the steel with the embossments at coating in situ. The sheet was then incorporated in a multi-layer steel gasket. It was found that the coating performed well in micro-sealing.

In order to form the second illustrative coating, the following were mixed together:

- (a) 200g of chemically-exfoliated vermiculite particles as mentioned at (a) of the first example.
- (b) 20g of graphite flake particles as mentioned at (b) of the first example.
- (c) 40g of silicone resin as mentioned at (e) of the first example.
- (d) 20g of water.

The mixture of the second example was sprayed on to the surface of a stainless steel sheet, dried, embossed and tempered in the same way as is described above in relation to the first illustrative example.

In order to form the third illustrative example, the following were mixed together.

- (a) 50g of chemically exfoliated vermiculite as mentioned in the first example.
- (b) 30g of methyl silicone resin emulsion (M50 E from Wacker). This was a suspension in water at 50% solids and provided an organic polymer binder.
- (c) 5g of lithium silicate as disclosed in the first example.
- (d) 5g of graphite flake particles as disclosed in the first example.
- (e) 5g of mica particles as disclosed in the first example.
- (f) 0.25g of aluminium powder as disclosed in the first example.
- (g) 30g of water.

The mixture of the third example was sprayed, embossed, and tempered in the same way as the first two examples.

The gasket coatings formed by the first, second and third illustrative methods all gave enhanced sealing coatings which were capable of micro-sealing at temperatures above 300°C.

## CLAIMS

- 1 A sealing-enhancing coating for a gasket or a portion of a gasket, characterised in that the coating comprises flaky particles of chemically exfoliated vermiculite, at least 90% by weight of said particles having a thickness of no more than 30 microns, and no dimension greater than 1mm, the particles forming 10 to 90 wt% of the coating, the coating also comprising 50 to 10 wt% of an organic polymer binder which is heat resistant to at least 300°C.
- 2 A coating according to claim 1, characterised in that the polymer binder is a silicon-containing polymer.
- 3 A coating according to claim 2, characterised in that the polymer binder is a silicone.
- 4 A coating according to claim 2, characterised in that the polymer binder is a siliconate.
- 5 A coating according to claim 1, characterised in that the polymer binder is selected from PTFE, phenolics, and fluoroelastomers.
- 6 A coating according to any one of claims 1 to 5, characterised in that the coating contains more of the organic polymer binder by weight than of the chemically exfoliated vermiculite.
- 7 A coating according to any one of claims 1 to 6, characterised in that the coating also comprises particles of a solid lubricant.
- 8 A coating according to any one of claims 1 to 7, characterised in that the coating also comprises a flaky filler.

- 9 A coating according to any one of claims 1 to 8, characterised in that the coating also comprises a supplementary inorganic binder.
- 10 A coating according to claim 9, characterised in that the supplementary inorganic binder is lithium silicate.
- 11 A coating according to any one of claims 1 to 4, characterised in that the coating also comprises a waterproofing agent acting on at least one of the chemically exfoliated vermiculite and the supplementary inorganic binder.
- 12 A coating according to any one of claims 1 to 11, characterised in that the coating has a thickness up to 80 microns.
- 13 A coating according to any one of claims 1 to 12, characterised in that the coating has a density of below 70% of the theoretical density of the material forming the coating.
- 14 A method of forming a gasket characterised in that the method comprises applying a coating according to any one of claims 1 to 13 to at least a portion of a metal sheet, embossing the metal sheet with the coating to form at least one resilient ridge therein with the coating extending across said ridge, and heating the embossed sheet to a temperature of at least 350°C to temper said sheet.

# **DECLARATION AND POWER OF ATTORNEY**

As below-named inventors, being duly sworn, We depose and say that our residence, address and citizenship are as stated below. We believe We are the original, first and joint inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled

GASKET COATING

\_\_\_\_\_, the specification of which is attached hereto. We hereby state that We have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. We acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, section 1.56(a).

We hereby claim foreign priority benefits under Title 35, United States Code, section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority date is claimed: \* PCT/GB99/00491 filed 15 FEBRUARY 1999

## **PRIOR FOREIGN APPLICATION(S) \***

Application No:	9804949.7	Application No:	9826737.0
Country:	UNITED KINGDOM	Country:	UNITED KINGDOM
Date of Filing:	10 MARCH 1998	Date of Filing:	7 DECEMBER 1998

We hereby claim the benefit under Title 35, United States Code, section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, section 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, section 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

<u>(Application Serial No.)</u>	<u>(Filing Date)</u>	<u>(Status-Patented/Pending/Abandoned)</u>
<u>(Application Serial No.)</u>	<u>(Filing Date)</u>	<u>(Status-Patented/Pending/Abandoned)</u>

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

We hereby appoint Jon E. Shackelford, Reg. No. 36,003, and Robert L. Stearns, Reg. No. 36,937 registered Patent Attorneys, as our attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. We request the Patent and Trademark Office to direct all correspondence and telephone calls relative to this application to Robert L. Stearns, 5291 Colony Drive North, Saginaw, Michigan 48603, Phone: 517-799-5300.

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